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Nonrelativistic energies for the low-lying states of lithium are calculated using the variational method in Hylleraas coordinates. Variational eigenvalues for the infinite nuclear mass case with up to 34 020 terms are −7.478 060 323 910 147(1) a.u. for $1s^2 2s\ ^2S$, −7.354 098 421 444 37(1) a.u. for $1s^2 3s\ ^2S$, −7.318 530 845 998 91(1) a.u. for $1s^2 4s\ ^2S$, −7.410 156 532 652 41(4) a.u. for $1s^2 2p\ ^2P$, and −7.335 523 543 524 688(3) a.u. for $1s^2 3d\ ^2D$. The selection of the minimum set of angular momentum configurations is discussed, with the $2P$ and $3D$ states as examples to demonstrate the impact of various configurations on the variational energies. It is shown by numerical example that the second spin function (i.e., coupled to form a triplet intermediate state) has no significant effect on either the variational energies or the spin-dependent Fermi contact term. Results of greatly improved accuracy for the Fermi contact term are presented for all the states considered.

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I. INTRODUCTION

The ultimate aim of theoretical atomic spectroscopy is to match or exceed the state of the art for accuracy in spectroscopic measurements. A comparison with the measurements then yields tests of fundamental theory, or new values for physical parameters such as fundamental constants or properties of the nucleus. It is currently not possible to achieve this goal of accuracy for many-electron atoms, even in the nonrelativistic limit, but it is possible for hydrogen, helium, and more recently also for lithium.

The most accurate results are achieved for two- and three-electron atoms by using the Rayleigh-Ritz variational method in Hylleraas coordinates. Though many difficulties still remain, significant advances have been achieved in the past two decades [1–9]. Especially in the past five years, the rate of progress has accelerated. For example, the ground-state energy of lithium has been calculated to 14 digit accuracy [8,9] and similarly for the $3S$ state [9]. Needless to say, these advances are closely correlated with the progress of computer technology. Basis sets containing as many as 27 000 terms were used in our recent work [9]. At this level, parallel processing becomes a necessity.

Other competitive methods are also under development. Sims and Hagstrom [10] used the Hy-CI (Hylleraas-configuration-interaction) method to calculate the ground-state energy of lithium to be −7.478 060 323 452 a.u. with 16 764 basis functions. Stanke *et al.* [11] used a method based on explicitly correlated Gaussian basis functions [12] to calculate the ground-state energy of lithium to −7.478 060 323 81 a.u. with 10 000 terms. These two results are both very accurate, but still several orders of magnitude less than the most accurate one obtained by using pure Hylleraas coordinates. This verifies that a variational method based on Hylleraas coordinates is still the most accurate method for solving the Schrödinger equation for two- and three-electron atoms.

One of the problems exhibited by Hylleraas basis sets is that, as the basis set is enlarged, it tends to develop a near linear dependence and numerical instability. To avoid this problem, Yan and Drake [2] (see also McKenzie and Drake [1]) introduced Hylleraas basis sets partitioned into multiple sectors with different distance scales that are individually optimized for each sector. These basis sets have been verified to be very efficient and stable in practical calculations [2–6]. In our recent paper [9], we made a slight modification to this method of choosing the basis sets and found that the new method is more efficient than the old one, and is still stable. The modifications involved subdividing one sector and truncating the terms in another, but this remains a matter of trial and error with few general rules to guide one's intuition. In particular, rules that appear to be true for small basis sets may no longer hold for large basis sets.

One issue that has not been adequately explored is the role of the second spin function. As well known, a spin-doublet state of lithium can be formed by coupling a third electron to either an intermediate singlet pair, or an intermediate triplet pair. Usually just the former is used in calculations. The impact of not including the latter triplet has been studied by many authors [13–17]. Their common conclusion is that including the triplet spin coupling explicitly will not enhance the convergence of the energy significantly, but it will strongly affect the expectation values of other operators which are spin dependent, such as the Fermi contact term. In this paper, we will give an argument to show that the triplet spin wave function is indispensable for the correct wave function of the system, though the energy is not very sensitive to it.

A further problem concerns the selection of angular momentum configurations for non-S states. The problem is well studied for two-electron systems in Hylleraas coordinates by Breit [18], Schwartz [19], and Drake [20], but for the three-electron case little had been published before the work of Harris [21] in 2005. In the present paper, we reinvestigate this problem and take the $2P$ and $3D$ states of lithium as examples to demonstrate the impact of various angular momentum configurations on the energy levels.

The rest of the paper is organized as follows. Section II discusses the overall form of the variational wave function, and especially the partitioning of the radial part into sectors with individually optimized distance scales. Section III presents a general discussion of the various angular couplings that are required for completeness of the variational basis set, and Sec. IV presents results for the $2P$ and $3D$ states to illustrate the role played by different angular momentum couplings. Section V studies in detail the effect of the second spin function on both the energies and the spin-dependent Fermi contact term. Finally, Sec. VI contains a brief summary of the results and their significance.

II. CONSTRUCTION OF BASIS SETS

For the sake of completeness, we briefly describe the structure of variational basis sets, based on our early work [2]. Further modifications to obtain better convergence of energy eigenvalues will be discussed in Secs. III and V.

The variational wave function is a linear combination of terms of the form (in atomic units throughout)

$$\psi = \mathcal{A}(\phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)), \tag{1}$$

where

$$\phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1-\beta r_2-\gamma r_3} \times \mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\chi_1 \tag{2}$$

and

$$\begin{aligned}\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}&(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\\ &= r_1^{\ell_1} r_2^{\ell_2} r_3^{\ell_3} \sum_{m_i} \langle \ell_1 m_1;\ell_2 m_2|\ell_1\ell_2;\ell_{12}m_{12}\rangle \\ &\quad\times \langle \ell_{12}m_{12};\ell_3 m_3|\ell_{12}\ell_3;LM\rangle \\ &\quad\times Y_{\ell_1 m_1}(\mathbf{r}_1)Y_{\ell_2 m_2}(\mathbf{r}_2)Y_{\ell_3 m_3}(\mathbf{r}_3)\end{aligned} \tag{3}$$

is the vector-coupled product of spherical harmonics for the three electrons to form a state of total angular momentum L and z component M,

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \tag{4}$$

is the spin function with the total spin $1/2$, and

$$\mathcal{A} = (1) - (12) - (13) - (23) + (123) + (132) \tag{5}$$

is the three-particle antisymmetrizer. The quantities r_i, $i = 1,2,3$ are the radial coordinates for the three electrons, and the $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ are the interparticle coordinates. The angular momenta ℓ_i are chosen according to

$$\begin{aligned}(\ell_1,\ell_2,\ell_3) &= (0,0,0)_A \quad \text{for } S \text{ states},\\ (\ell_1,\ell_2,\ell_3) &= (0,0,1)_A,(0,1,0)_B \quad \text{for } P \text{ states},\\ (\ell_1,\ell_2,\ell_3) &= (0,0,2)_A,(0,1,1)_B \quad \text{for } D \text{ states}.\end{aligned} \tag{6}$$

As described previously [2], all terms in Eq. (2) are nominally included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega \tag{7}$$

and the convergence of the eigenvalues is studied as Ω is progressively increased. However, terms that may potentially cause near linear dependence are omitted. For example, if $\ell_1 = \ell_2$ and $\alpha \approx \beta$, then terms with $j_1 > j_2$ are omitted, as well as terms with $j_1 = j_2$ when $j_{23} > j_{31}$. The presence of the near-linear dependency problem in a basis set may be detected by diagonalizing the positive-definite overlap matrix to check for abnormally small or negative eigenvalues. Furthermore, the first sector $(0,0,L)_A$ is further divided into five subsectors according to correlations among the three electrons

$$\begin{aligned}&\text{sector 1}: \quad \text{all } j_{12}, \quad j_{23}=0, \quad j_{31}=0,\\ &\text{sector 2}: \quad \text{all } j_{12}, \quad j_{23}=0, \quad j_{31}\neq 0,\\ &\text{sector 3}: \quad \text{all } j_{12}, \quad j_{23}\neq 0, \quad j_{31}=0,\\ &\text{sector 4}: \quad j_{12}=0, \quad j_{23}\neq 0, \quad j_{31}\neq 0,\\ &\text{sector 5}: \quad j_{12}\neq 0, \quad j_{23}\neq 0, \quad j_{31}\neq 0.\end{aligned} \tag{8}$$

Thus the basis sets contain five sectors for S states and six sectors for P and D states including $(0,1,0)_B$ or $(0,1,1)_B$. The size of each sector is separately determined by assigning to each an Ω_i according to

$$\begin{aligned}\{\Omega_1,\Omega_2,\Omega_3,\Omega_4,\Omega_5\} &= \{\Omega,\Omega,\Omega,\Omega,\Omega\}, \quad L=0\\ \{\Omega_1,\Omega_2,\Omega_3,\Omega_4,\Omega_5,\Omega_6\} &= \{\Omega,\Omega,\Omega,\Omega,\Omega,\Omega-2\}, \quad L=1,2\end{aligned}$$

III. COMPLETENESS OF HYLLERAAS-TYPE BASIS SETS

For the S states of two-electron atomic systems, the completeness of a Hylleraas-type basis set has been proved rigorously by Klahn and Bingel [22]. Their detailed proof is lengthy, but the problem can be simply understood from the viewpoint of configuration interaction involving a multipole expansion. By definition r_{12}^{2n} can be written in the form

$$r_{12}^{2n} = \left[r_1^2 + r_2^2 - 2\mathbf{r}_1\cdot\mathbf{r}_2\right]^n, \tag{9}$$

and $\mathbf{r}_1\cdot\mathbf{r}_2 = r_1 r_2 \cos\theta_{12}$, where θ_{12} is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. Thus the right-hand side of Eq. (9) contains terms up to $\cos^n\theta_{12}$, which can be reexpressed as finite linear combinations of Legendre polynomials up to $P_n(\cos\theta_{12})$. Each Legendre polynomial can in turn be expanded into multipoles according to the spherical harmonic addition theorem

$$P_q(\cos\theta_{12}) = \frac{4\pi}{2q+1}\sum_{m=-q}^{q}(-1)^m Y_{q-m}(\mathbf{r}_1)Y_{qm}(\mathbf{r}_2). \tag{10}$$

Since $\cos\theta_{12}$ is rotationally invariant, so also is the sum over spherical harmonics on the right-hand side. Thus each term $P_q(\cos\theta_{12})$ is equivalent to the coupling of two electrons of angular momentum q to form an S state; and so the even powers of r_{12} alone, when multiplied into the uncorrelated wave function with independent variational parameters, are equivalent to the partial wave expansion of a configuration interaction (CI) wave function for an S state, and a CI wave function is known to be complete when all partial waves are included. The angular momentum couplings generated are thus of the form $(ss')\,{}^1S + (pp')\,{}^1S + (dd')\,{}^1S + \cdots$, with independent variational coefficients for each term. The odd powers of r_{12} greatly accelerate the rate of convergence because they are suited to a representation of the electron cusp condition along the line $r_1 = r_2$. For an example, see Ref. [23]. The problem of completeness for the three-electron case can be understood in a similar way, as discussed further below.

For the non-S states of two-electron atomic systems, the problem of the completeness of Hylleraas coordinates has been

studied by Breit [18], Schwartz [19], and Drake [20]. The common conclusion of these authors is that, because r_{12}^n is included explicitly in the Hylleraas-type basis functions, the addition of at most $[L/2]$ angular momentum configurations is sufficient to achieve completeness in the limit as the basis set is enlarged, where $[L/2]$ denotes "greatest integer in." A detailed rule for selecting these additional angular momentum configurations has been given by Drake [20]. For a singly excited state of angular momentum L, the minimum (ℓ_1,ℓ_2) configurations needed in the basis set are those with $\ell_1+\ell_2=L$, and $\ell_1 \leqslant \ell_2$. As a simple example, for $L=2$ the essential angular couplings are of the form $sd\ ^1D$ and $pp'\ ^1D$, and similarly for the triplets.

For the non-S states of three-electron atomic systems, the problem of the completeness of Hylleraas coordinates was recently discussed by Harris [21], building on the earlier work of Schwartz [19] for the two-electron case. We first summarize the main points of Schwartz and Harris and then give the necessary angular momentum configurations for $2P$ and $3D$ states of lithium.

The basic form of the Hylleraas-type basis functions for three-electron systems is described by Eq. (2) and the angular part of the functions is described by Eq. (3). As for the two-electron case, we first consider the additional angular functions that are generated when the basic function in Eq. (3) is multiplied by powers of the r_{ij} coordinates. It follows from the triangular rule for angular momentum coupling and parity selection rules that

$$\cos\theta Y_{\ell,m}(\theta,\phi) = A_{\ell,m}^{\ell-1} Y_{\ell-1,m}(\theta,\phi) + A_{\ell,m}^{\ell+1} Y_{\ell+1,m}(\theta,\phi). \tag{11}$$

The only nonvanishing values for the coefficients $A_{\ell,m}^{\ell'}$ are

$$A_{\ell,m}^{\ell'} = (-1)^m[(2\ell+1)(2\ell'+1)]^{1/2} \times \begin{pmatrix} 1 & \ell & \ell' \\ 0 & m & -m \end{pmatrix} \begin{pmatrix} 1 & \ell & \ell' \\ 0 & 0 & 0 \end{pmatrix} \tag{12}$$

expressed in terms of $3j$ symbols [24] with $\ell' = \ell \pm 1$. The general form for $\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2$ acting on the initial $\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}$ is thus

$$\begin{aligned}(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2)\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3} &= C_1\mathcal{Y}^{LM}_{(\ell_1-1,\,\ell_2-1)\ell_{12},\ell_3} + C_2\mathcal{Y}^{LM}_{(\ell_1-1,\,\ell_2+1)\ell_{12},\ell_3} \\ &\quad + C_3\mathcal{Y}^{LM}_{(\ell_1+1,\,\ell_2-1)\ell_{12},\ell_3} + C_4\mathcal{Y}^{LM}_{(\ell_1+1,\,\ell_2+1)\ell_{12},\ell_3},\end{aligned} \tag{13}$$

where the C_i are constants, and all $\ell_i \pm 1$ are non-negative. Thus successive powers of $\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2$ generate a wide variety of configurations $((\ell_1',\ell_2')\ell_{12},\ell_3; LM)$, but they are not all linearly independent because of the fixed C_i coefficients in Eq. (13). Similarly powers of $\hat{\mathbf{r}}_2 \cdot \hat{\mathbf{r}}_3$ generate configurations of the form $((\ell_1,\ell_2')\ell_{12}',\ell_3'; LM)$, but again they are not all linearly independent. For a state with definite total angular momentum L, only those configurations satisfying the following conditions need be included explicitly in Hylleraas bases [21]:

$$\ell_1+\ell_2+\ell_3 = L \quad \text{for parity } (-1)^L, \tag{14}$$

$$\ell_1+\ell_2+\ell_3 = L+1 \quad \text{for parity } (-1)^{(L+1)}. \tag{15}$$

Another problem that should be emphasized is that the coupling schemes of angular momenta for three-body systems are not unique [24]. The three distinct coupling schemes are (in an obvious notation) $|(\ell_1,\ell_2)\ell_{12}\,\ell_3; L\,M\rangle$, $|\ell_1(\ell_2,\ell_3)\ell_{23}; L\,M\rangle$, and $|(\ell_1,\ell_3)\ell_{13}\,\ell_2; L\,M\rangle$. In general, there are multiple possible values for the intermediate angular momenta ℓ_{12}, ℓ_{23}, and ℓ_{13}. In fact, these three-coupling schemes should be physically equivalent. This is ensured by the possibility of unitary transformations among these three schemes. For example, there is a relationship between the state vectors of the first and second according to the recoupling transformation

$$\begin{aligned}&|\ell_1(\ell_2,\ell_3)\ell_{23}; L\,M\rangle \\ &\quad = (-1)^{\ell_1+\ell_2+\ell_3+L}\sum_{\ell_{12}'}\sqrt{(2\ell_{12}'+1)(2\ell_{23}+1)} \\ &\qquad \times \begin{Bmatrix} \ell_1 & \ell_2 & \ell_{12}' \\ \ell_3 & L & \ell_{23} \end{Bmatrix} |(\ell_1,\ell_2)\ell_{12}'\,\ell_3; L\,M\rangle,\end{aligned} \tag{16}$$

expressed in terms of the standard $6j$ symbols [24]. It can be seen from the above equation that the transformation from the first to the second scheme can be completed only if all possible values of ℓ_{12} are included in the basis set. So, the values of the intermediate angular momenta (ℓ_{12}, or ℓ_{23}, or ℓ_{13}) are important.

TABLE I. Angular momentum configurations for P states (odd parity) of lithium.

No.	ℓ_1	ℓ_2	ℓ_{12}	ℓ_3	L	M
1	0	0	0	1	1	0
2	0	1	1	0	1	0
3	1	0	1	0	1	0

IV. RESULTS FOR THE $2P$ AND $3D$ STATES

Following the discussions of the preceding section, we list the necessary angular momentum configurations for $2P$ and $3D$ states of lithium in Tables I and II, respectively. For the $2P$ state, there are three configurations in total. As pointed out by Yan and Drake [2], the energy of the $1s^2 2p\ ^2P$ state would converge to a wrong value if only the first configuration in Table I were used. This is evidence of the incompleteness of the basis set. In Table III, we list the energies of the $2P$ state calculated using two configurations and three configurations. The results calculated using two configurations are quoted from our recent paper [9]. The variational basis set for the calculations using three configurations is constructed as follows: the whole basis set is divided into seven sectors, and the radial parts of the first four sectors are generated according to the basic manner described previously, namely, formula (8).

TABLE II. Angular momentum configurations for D states (even parity) of lithium.

No.	ℓ_1	ℓ_2	ℓ_{12}	ℓ_3	L	M
1	0	0	0	2	2	0
2	0	1	1	1	2	0
3	0	2	2	0	2	0
4	1	0	1	1	2	0
5	2	0	2	0	2	0
6	1	1	2	0	2	0

TABLE III. Convergence study for the nonrelativistic energy of lithium in the $1s^2 2p\ ^2P$ state, calculated using two and three angular momentum configurations, respectively, and with the second spin function χ_2. Units are atomic units, and $\Omega = \infty$ denotes the extrapolated value.

Ω	N	$E(\Omega)$	$R(\Omega)$
	$(\ell_1,\ell_2,\ell_3) = (0,0,1), (0,1,0)$ with χ_1 only		
10	3024	−7.410 156 531 219 66	
11	4824	−7.410 156 532 310 89	
12	7440	−7.410 156 532 558 34	4.409
13	11118	−7.410 156 532 625 75	3.670
14	16164	−7.410 156 532 640 83	4.470
15	23004	−7.410 156 532 648 43	1.983
16	30224	−7.410 156 532 650 66	3.402
	$(\ell_1,\ell_2,\ell_3) = (0,0,1), (0,1,0), (1,0,0)$ with χ_1 only		
8	1016	−7.410 156 502 496 189	
9	1870	−7.410 156 529 965 265	
10	3300	−7.410 156 532 354 927	11.49
11	5600	−7.410 156 532 619 679	9.026
12	9170	−7.410 156 532 647 379	9.557
13	14532	−7.410 156 532 651 514	6.698
14	22400	−7.410 156 532 652 175	6.257
15	33600	−7.410 156 532 652 360	3.575
∞		−7.410 156 532 652 4(1)	
	$(\ell_1,\ell_2,\ell_3) = (0,0,1), (0,1,0), (1,0,0)$ with χ_1 and χ_2		
5	153	−7.410 148 566 764 002	
6	385	−7.410 155 955 712 337	
7	888	−7.410 156 484 860 455	13.96
8	1878	−7.410 156 528 148 006	12.22
9	3692	−7.410 156 532 067 689	11.04
10	6828	−7.410 156 532 624 245	7.04
11	11950	−7.410 156 532 650 209	21.43
12	20000	−7.410 156 532 652 104	13.69
13	32200	−7.410 156 532 652 370	7.13
∞		−7.410 156 532 652 41(4)	
	Other calculations		
8	1715	−7.410 156 518 4[a]	
12		−7.410 156 532 628 6[b]	
∞		−7.410 156 532 665(14)[b]	

[a] Yan *et al.* [2].
[b] Puchalski *et al.* [6].

The radial part of the fifth sector is generated by the formula

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega - 4, \tag{17}$$

but terms with $j_1 > j_2$ and $j_1 = j_2$ when $j_{23} > j_{31}$ are omitted to avoid unnecessary duplication and potential linear dependence. The radial parts of the sixth sector and the seventh sector are also generated by formula (17), but no terms are omitted here. The first five sectors are assigned the angular momentum configuration $(\ell_1,\ell_2,\ell_3) = (0,0,1)$, and the sixth and seventh sectors are assigned configurations $(\ell_1,\ell_2,\ell_3) = (0,1,0)$ and $(\ell_1,\ell_2,\ell_3) = (1,0,0)$, respectively.

As can be seen from Table III, the energies decrease significantly when the third configuration is added, and the energy convergence ratios $R(\Omega)$ are much larger (i.e., faster convergence) when using three configurations than when using two configurations. $R(\Omega)$ is defined in terms of the ratio of successive differences by

$$R(\Omega) = \frac{E(\Omega) - E(\Omega-1)}{E(\Omega-1) - E(\Omega-2)}, \tag{18}$$

and so it immediately reveals the pattern of convergence. The case $R =$ constant is the ideal case corresponding to geometric convergence. The results in Table III demonstrate that the third configuration $(\ell_1,\ell_2,\ell_3) = (1,0,0)$ is important for calculations of the $2P$ state of lithium.

For the $3D$ state of lithium, according to our analysis, there are in total six necessary angular momentum configurations. For completeness, we add these one by one and study their impact on the energy of the $3D$ state, as listed in Table IV. It can be seen from the table that with only one angular momentum configuration (0,0,2), the energy of the $1s^2 3d\ ^2D$ state converges to −7.335 523 087 a.u., in which only the first seven figures are correct. When two configurations (0,0,2) and (0,1,1) are used, the variational energy decreases to −7.335 523 543 078, in which the first ten figures are correct. When three configurations (0,0,2), (0,2,0), and (0,1,1) are used, the variational energy with 25 788 basis functions is −7.335 523 543 523 941 a.u., with almost thirteen correct figures. When four configurations (0,0,2), (0,2,0), (2,0,0), and (0,1,1) are used, the variational energy with 30 000 basis functions is −7.335 523 543 524 386 a.u., which has thirteen correct figures. When five configurations (0,0,2), (0,2,0), (2,0,0), (0,1,1), and (1,0,1) are used, the variational energy with 32 760 basis functions is −7.335 523 543 524 685 a.u., which has fourteen or fifteen correct figures. It is significant that the $R(\Omega)$ convergence ratios are much larger with five configurations than they are for the other cases with fewer configurations. We find that adding the sixth and final configuration (1,1,0) in Table II does not further lower the energy significantly, and so we do not list the results explicitly in Table IV.

V. EFFECT OF THE SECOND SPIN FUNCTION ON ENERGIES AND SPIN-DEPENDENT MATRIX ELEMENTS

As mentioned in the Introduction, there are two independent spin wave functions for the double states of lithium,

$$\chi_1(1,2,3) = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3), \tag{19}$$

$$\chi_2(1,2,3) = 2\alpha(1)\alpha(2)\beta(3) - \beta(1)\alpha(2)\alpha(3) - \alpha(1)\beta(2)\alpha(3). \tag{20}$$

The physical meaning of χ_1 is that electrons 1 and 2 are first coupled to a spin single state $S_{12} = 0$, and the result coupled with electron 3 to give a final state with total spin $S = 1/2$ and z component $S_z = 1/2$. χ_2 means that electrons 1 and 2 are first coupled to a spin triplet state $S_{12} = 1$, and the result coupled with electron 3 to give a final state with total spin $S = 1/2$ and z component $S_z = 1/2$. Larsson had given detailed discussions about the necessity of the second spin wave function in the calculations of the energy levels of lithium [13]. His conclusion is that if the basis set contains the terms generated by the operator

$$\mathcal{A}\{(13)\phi\chi_1\}, \tag{21}$$

TABLE IV. Convergence study for the nonrelativistic energy of lithium in the $1s^2 3d\ ^2D$ state, calculated using different angular momentum configurations. Units are atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$
		$(\ell_1,\ell_2,\ell_3) = (0,0,2)$	
7	288	−7.335 522 846 909 011	
8	570	−7.335 523 005 011 643	
9	1050	−7.335 523 078 299 127	2.157
10	1830	−7.335 523 086 314 969	9.142
11	3040	−7.335 523 087 718 336	5.711
		$(\ell_1,\ell_2,\ell_3) = (0,0,2), (0,1,1)$	
10	1785	−7.335 523 540 669 860	
11	3045	−7.335 523 542 483 543	
12	4970	−7.335 523 542 882 444	4.471
13	7820	−7.335 523 543 001 790	3.342
14	11952	−7.335 523 543 052 819	2.338
15	17780	−7.335 523 543 078 357	2.018
		$(\ell_1,\ell_2,\ell_3) = (0,0,2), (0,1,1), (0,2,0)$	
9	1722	−7.335 523 541 259 572	
10	3180	−7.335 523 543 125 368	
11	5548	−7.335 523 543 444 753	5.841
12	9240	−7.335 523 543 510 569	4.852
13	13800	−7.335 523 543 520 135	6.880
14	16960	−7.335 523 543 522 726	3.692
15	25788	−7.335 523 543 523 941	2.132
		$(\ell_1,\ell_2,\ell_3) = (0,0,2), (0,1,1), (0,2,0), (2,0,0)$	
8	704	−7.335 523 524 776 523	
9	1428	−7.335 523 541 000 464	
10	2700	−7.335 523 543 043 150	7.942
11	4888	−7.335 523 543 477 152	4.706
12	8400	−7.335 523 543 512 381	12.31
13	13832	−7.335 523 543 522 043	3.646
14	21966	−7.335 523 543 524 045	4.824
15	30000	−7.335 523 543 524 386	5.876
		$(\ell_1,\ell_2,\ell_3) = (0,0,2), (0,1,1), (0,2,0), (2,0,0), (1,0,1)$	
8	780	−7.335 523 524 256 807	
9	1638	−7.335 523 541 397 026	
10	3180	−7.335 523 543 374 304	8.688
11	5810	−7.335 523 543 510 671	14.49
12	10115	−7.335 523 543 523 117	10.95
13	16835	−7.335 523 543 524 362	9.997
14	26955	−7.335 523 543 524 655	4.177
15	32760	−7.335 523 543 524 685	9.820
∞		−7.335 523 543 524 688(3)	
		Other calculations	
8	1673	−7.335 523 540 35[a]	
∞		−7.335 523 541 10(43)[a]	
	4000	−7.335 523 542 97[b]	

[a] Yan *et al.* [2].
[b] Sharkey *et al.* [25].

then, according to this argument, the second spin function need not be explicitly included. Here, $\mathcal{A}$ is the three-particle antisymmetrizer and (13) denotes the exchange of electron 1 and electron 3 operating on ϕ (the orbital part of the wave function). The energy lowering when $\mathcal{A}\{\phi\chi_2\} = \mathcal{A}\{(13)\phi\chi_1\}$ is included would then be small.

In the following two sections, we present extensive numerical tests of the effect of the second spin function on energies and expectation values of spin-dependent operators, such as the Fermi contact term.

A. Second spin function and energies

In Table V, we list the energies for the ground state of lithium calculated using only χ_1, only χ_2, and both χ_1 and χ_2, respectively. The energies calculated using only χ_1 are cited from our recent paper [9]. The radial parts of the basis set for using χ_2 are obtained by exchanging j_1 with j_3 and j_{12} with j_{23} of the radial parts of the basis set for using χ_1. The radial part of the basis set for using both χ_1 and χ_2 is divided into six sectors. The first four sectors are constructed according to the basis manner described in Sec. II, namely, formula (8). The fifth sector is generated by the following manner:

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega - 3, \qquad (22)$$

but terms like $j_1 > j_2$ and $j_1 = j_2$ when $j_{23} > j_{31}$ are omitted for avoiding the potential linear dependence. The sixth sector is also generated by Eq. (22), but when $\Omega < 10$ the terms that should be omitted are the same as the fifth sector; when $\Omega \geqslant 10$, terms like $j_1 > j_3$ and $j_{12} > j_{31}$ when $j_1 = j_3$ are omitted.

It can be seen from Table V that the energy of the ground state of the lithium can be calculated to −7.478 060 323 910 134 a.u. with 265 20 basis functions only using χ_1, and it can be calculated to −7.478 060 323 909 942 a.u. with 265 20 basis functions only using χ_2. When both χ_1 and χ_2 are used, the energy can be calculated to −7.478 060 323 910 146 894 a.u. with 340 20 basis functions. Comparing these results, we can make the conclusion that the nonrelativistic energy levels of lithium do not depend on the spin wave functions. No matter whether χ_1 or χ_2 or both χ_1 and χ_2 are used, the energy of the ground state of the lithium converges to the same limit. However, if both χ_1 and χ_2 are used, the energy converges slightly more quickly. In Tables VI and VII, we list the energies of $3S$–$6S$ states of lithium which are calculated using χ_1 and both χ_1 and χ_2, respectively. Here also, adding the second spin wave function slightly improves the convergence ratios.

We also explored the effect of the second spin function for the $2P$ state, using a basis set divided into ten sectors. The first seven sectors were the same as those in the one-spin case, and with the same Ω for the highest sum of powers. The last three sectors (i.e., 8, 9, and 10) were assigned the second spin function and angular momentum configurations (0,0,1), (0,1,0), and (1,0,0), respectively, but with the smaller sum of powers $\Omega_2 = \Omega - 3$ [cf. Eq. (22)]. In addition, the terms in the eighth sector were truncated such that terms with $j_1 \geqslant j_2$ when $j_{23} > j_{31}$ were omitted. The results are included in Table III. As can be seen, the pattern of convergence is unusually smooth for this case, and yields the best variational bound for the $2P$ state. The results with and without the second spin function agree with each other within the estimated uncertainty.

B. Second spin function and the Fermi contact term

For expectation values of spin-dependent operators, such as the Fermi contact term, one might argue that the effect of

TABLE V. Convergence study for the nonrelativistic energy of Li in the ground state, calculated using only the first spin wave function χ_1, the second spin wave function χ_2, and both spin wave functions χ_1 and χ_2, respectively. N is the number of terms, and $\Omega = \infty$ denotes the extrapolated value. Units are atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$
		With only χ_1	
10	3910	−7.478 060 323 880 889	
11	6039	−7.478 060 323 905 362	
12	9056	−7.478 060 323 909 450	5.986
13	13248	−7.478 060 323 909 950	8.174
14	18935	−7.478 060 323 910 102	3.290
15	26520	−7.478 060 323 910 134	4.679
		With only χ_2	
10	3910	−7.478 060 323 491 870	
11	6039	−7.478 060 323 825 035	
12	9056	−7.478 060 323 891 747	4.994
13	13248	−7.478 060 323 902 848	6.009
14	18935	−7.478 060 323 908 907	1.832
15	26520	−7.478 060 323 909 791	6.851
		With both χ_1 and χ_2	
10	5082	−7.478 060 323 905 585 516	
11	7992	−7.478 060 323 909 524 819	
12	12168	−7.478 060 323 910 044 374	7.582
13	18108	−7.478 060 323 910 127 997	6.213
14	24552	−7.478 060 323 910 144 868	4.956
15	34020	−7.478 060 323 910 146 894	8.327
∞		−7.478 060 323 910 147(1)	
Sims *et al.* [10]	16764	−7.478 060 323 452	
Stanke *et al.* [11]	10000	−7.478 060 323 81	
Yan *et al.* [4]	9577	−7.478 060 323 892 4	
Puchalski *et al.* [8]	30632	−7.478 060 323 910 097	
Puchalski *et al.* [8]	∞	−7.478 060 323 910 2(2)	

TABLE VI. Convergence study for the nonrelativistic energies of Li in the $1s^2 3s\ ^2S$ and $1s^2 4s\ ^2S$ states, calculated using the spin wave function χ_1 and the spin wave functions χ_1 and χ_2, respectively. N is the number of terms, and $\Omega = \infty$ denotes the extrapolated value. Units are atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$	$E(\Omega)$	$R(\Omega)$
		$1s^2 3s\ ^2S$		$1s^2 4s\ ^2S$	
			With χ_1 only		
10	3910	−7.354 098 421 345 692		−7.318 530 845 805 121	
11	6039	−7.354 098 421 430 788		−7.318 530 845 973 819	
12	9056	−7.354 098 421 441 885	7.668	−7.318 530 845 994 767	8.053
13	13248	−7.354 098 421 443 757	5.928	−7.318 530 845 998 076	6.330
14	18935	−7.354 098 421 444 256	3.746	−7.318 530 845 998 783	4.679
15	26520	−7.354 098 421 444 313	8.792	−7.318 530 845 998 873	7.861
			With χ_1 and χ_2		
10	5082	−7.354 098 421 429 480 658		−7.318 530 845 949 424 961	
11	7992	−7.354 098 421 442 608 886		−7.318 530 845 993 305 012	
12	12168	−7.354 098 421 444 138 932	8.580	−7.318 530 845 998 086 597	9.176
13	18108	−7.354 098 421 444 332 016	7.924	−7.318 530 845 998 795 354	6.746
14	24552	−7.354 098 421 444 354 317	8.658	−7.318 530 845 998 889 685	7.513
15	34020	−7.354 098 421 444 364 045	2.292	−7.318 530 845 998 906 901	5.479
∞		−7.354 098 421 444 37(1)		−7.318 530 845 998 91(1)	
King [26]	1900	−7.354 098 355	1900	−7.318 530 816	
Sims *et al.* [10]	17180	−7.354 098 420 933	17072	−7.318 530 845 331	
Stanke *et al.* [11]	10000	−7.354 098 421 113			
Puchalski *et al.* [8]	15952	−7.354 098 421 442 66	15952	−7.318 530 845 990 3	
Puchalski *et al.* [8]	∞	−7.354 098 421 443 2(4)	∞	−7.318 530 845 994(2)	

TABLE VII. Convergence study for the nonrelativistic energies of Li in the $1s^2 5s\ ^2S$ and $1s^2 6s\ ^2S$ state, calculated using the spin wave function χ_1 and the spin wave functions χ_1 and χ_2, respectively. N is the number of terms and $\Omega = \infty$ denotes the extrapolated value. Units are atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$	$E(\Omega)$	$R(\Omega)$
		$1s^2 5s\ ^2S$		$1s^2 6s\ ^2S$	
			With χ_1 only		
10	3910	−7.303 551 578 555 033		−7.295 859 506 736 444	
11	6039	−7.303 551 579 159 207		−7.295 859 510 281 078	
12	9056	−7.303 551 579 216 794	10.49	−7.295 859 510 759 016	7.416
13	13248	−7.303 551 579 224 834	7.162	−7.295 859 510 827 607	6.967
14	18935	−7.303 551 579 226 329	5.377	−7.295 859 510 841 869	4.809
15	26520	−7.303 551 579 226 629	4.986	−7.295 859 510 843 625	8.126
			With χ_1 and χ_2		
10	5082	−7.303 551 578 888 417 980		−7.295 859 509 245 942 566	
11	7992	−7.303 551 579 198 474 278		−7.295 859 510 700 292 483	
12	12168	−7.303 551 579 223 521 339	12.37	−7.295 859 510 830 668 471	11.15
13	18108	−7.303 551 579 226 342 318	8.878	−7.295 859 510 842 332 362	11.17
14	24552	−7.303 551 579 226 649 253	9.190	−7.295 859 510 843 842 102	7.725
15	34020	−7.303 551 579 226 734 650	3.594	−7.295 859 510 844 131 039	5.225
∞		−7.303 551 579 226 77(4)		−7.295 859 510 844 19(6)	
King [26]	1900	−7.303 551 551		−7.295 859 384	
Sims *et al.* [10]	17072	−7.303 551 578 291		−7.295 859 509 943	
Puchalski *et al.* [8]	15952	−7.303 551 579 219 0		−7.295 859 510 808 3	
Puchalski *et al.* [8]	∞	−7.303 551 579 222(3)		−7.295 859 510 815(6)	

the second spin wave function may be more important. The circumstantial evidence presented by King [16,17] seemed to indicate that the rate of convergence was greatly accelerated by adding the second spin function, based on basis sets with 332 terms vs 602 terms with both spin functions.

In order to settle the question, we have carried out extensive calculations using only the first spin function, and both spin functions together. The uncorrected Fermi contact factor f_c is defined by

$$f_c = 4\pi \langle \Psi | \sum_{i=1}^{3} \delta(\mathbf{r}_i)\sigma_{zi} | \Psi \rangle, \tag{23}$$

where $\hbar\sigma_{zi}/2$ is the spin operator of electron i in the z direction, and Ψ is the nonrelativistic wave function of lithium for infinite nuclear mass. This is related to the full hyperfine structure coupling constant $A_{1/2}(\text{exp})$ by

$$A_{1/2}(\text{exp}) = 2(1 + a_e) C_{\text{rel}} C_M C_R C_{\text{QED}} \times 95.410\,67(7)\,\frac{\mu_I}{3I} f_c\ \text{MHz}, \tag{24}$$

where μ_I is the magnetic moment of the nucleus, a_e is the anomalous magnetic moment correction, C_{rel} is the relativistic correction factor, C_M and C_R are the finite nuclear mass and size correction factors, and C_{QED} is the QED correction factor other than the anomalous magnetic moment correction (see Ref. [27] for further details).

The results of calculations of f_c for the $2S$ and $3S$ states of lithium are shown in Table VIII. The ratios $R(\Omega)$ of successive differences indicate that the convergence is generally erratic, but the differences between successive calculations nevertheless progressively decrease. The significant point is that the number of figures that are correct are about the same for basis sets of approximately the same size. The final result is more accurate with two spin functions only because the total basis set size is larger. The final result for the $2S$ state of $f_c = 2.905\,968\,95(5)$ a.u. is in harmony with our previous value 2.905 922(50), and with the effective nonrelativistic result 2.905 89 extracted from the large-scale relativistic CI calculations of Yerokhin [29]. It seems clear that the larger value 2.908 56(8) a.u. obtained by Esquival *et al.* is overestimated. The results in Table VIII for the $3S$ state are in similarly good agreement with our previous calculations and those of Yerokhin [29]. The value with two spin functions has evidently converged to the very accurate result $f_c = 0.673\,380\,816(3)$ a.u. Previous experience with high precision Hylleraas calculations for helium [30] indicates that the accuracy for both states could be further improved by a factor of 20 or more by use of the Hiller-Sucher-Feinberg (HSF) [31] global operator. For wave functions of low accuracy, or for Gaussian basis sets [32], even larger improvements in accuracy have been obtained with both the HSF and Drachman [33] global operators.

Results for the higher-lying S states, the $2P$ state, and the $3D$ state are summarized in Table IX. For most cases, the results with one spin function and both spin functions agree within the estimated uncertainties, although the $2P$ state appears to be anomalous in this regard, undoubtedly due to the erratic nature of the convergence.

The conclusion from all the results taken together is that the second spin function has no direct effect on the final converged value of expectation values, even for spin-dependent operators such as f_c. However, the *rate* of convergence may depend on the strategy used to construct the variational wave function. The multiplicity of distance scales used in the present work for the spatial part appears to produce the same enhancement of convergence as including the second spin function explicitly,

TABLE VIII. Fermi contact term f_c for the Li $2S$ and $3S$ states, with and without the second spin function χ_2. N is the number of terms and $\Omega = \infty$ denotes the extrapolated value. Units are atomic units.

Ω	N	f_c	$R(\Omega)$	f_c	$R(\Omega)$
		$1s^2 2s\ ^2S$		$1s^2 3s\ ^2S$	
		With χ_1 only			
5	255	2.909 653 645 056		0.680 191 820 971	
6	500	2.906 774 702 366		0.674 102 759 251	
7	910	2.905 845 558 005	3.098	0.673 273 729 239	7.344
8	1580	2.906 015 663 946	−5.462	0.673 414 603 634	−5.884
9	2620	2.905 998 447 250	−9.880	0.673 412 297 822	−61.099
10	3910	2.905 952 999 341	0.378	0.673 384 394 853	0.083
11	6039	2.905 970 621 969	−2.578	0.673 377 420 547	4.000
12	9056	2.905 969 401 324	−14.43	0.673 381 377 367	−1.762
13	13248	2.905 969 443 355	−29.04	0.673 380 631 643	−5.306
14	18935	2.905 968 909 939	−7.879	0.673 380 926 602	−2.528
15	26520	2.905 968 946 277	−14.67	0.673 380 729 330	−5.678
∞		2.905 968 944(37)		0.673 380 81(19)	
		With χ_1 and χ_2			
5	270	2.901 676 269 089		0.676 996 860 796	
6	550	2.905 038 297 856		0.672 848 734 456	
7	1024	2.906 005 450 054	3.476	0.673 624 710 626	−5.345
8	1840	2.905 974 291 454	−31.03	0.673 327 460 084	−2.610
9	3125	2.905 987 258 807	−2.402	0.673 386 386 061	−5.044
10	5082	2.905 968 903 909	−0.706	0.673 382 187 111	−6.988
11	7992	2.905 969 903 592	−18.36	0.673 381 678 637	−2.263
12	12618	2.905 968 826 597	−0.928	0.673 380 436 264	−3.008
13	18188	2.905 968 925 663	−10.87	0.673 380 904 796	−2.643
14	26250	2.905 969 012 972	1.135	0.673 380 813 175	−4.135
15	34020	2.905 968 915 597	−0.897	0.673 380 816 397	−5.433
∞		2.905 968 967(52)		0.673 380 816(3)	
Yan *et al*. [27]		2.905 922(50)		0.673 41(5)	
Esquivel *et al*. [28]		2.908 56(8)			
Yerokhin [29]		2.905 89		0.673 36	

as observed by King [16,17]. This conclusion applies only to first-order perturbation corrections. The second spin function would play a crucial role in sums over virtual intermediate states for higher-order perturbation corrections due to spin-dependent operators.

VI. SUMMARY

In this paper, we discussed the completeness of the Hylleraas-type basis set for three-electron atomic systems, with the $2P$ and $3D$ states as examples to demonstrate the impact of the various angular moment configurations to the energy levels. We presented the most accurate nonrelativistic energies and wave functions available for the $2S$–$6S$, $2P$, and $3D$ states of lithium. It is well established in the literature that the energies are not sensitive to the second spin wave function, and that is fully confirmed in this work. What is not so well established is the role of the second spin function for spin-dependent operators. Contrary to previous work [16,17], our results show that the second spin function does not affect diagonal expectation values, such as the Fermi contact term, provided that there is sufficient flexibility in the spatial part of the variational wave function. The accuracy of this term is substantially improved for the $2S$–$6S$, $2P$, and $3D$ states of lithium. These results lay the foundation for improved calculations of corrections due to relativistic and QED effects, and applications to isotope shifts [4].

TABLE IX. Fermi contact term f_c for excited states of lithium, with and without the second spin function. Units are atomic units.

State	With χ_1 only	With χ_1 and χ_2
$4S$	0.253 973 48(2)	0.253 973 58(1)
$5S$	0.121 867 2(5)	0.121 867 22(1)
$6S$	0.067 594 6(1)	0.067 594 4(2)
$2P$	−0.214 617 83(6)	−0.214 617 75(2)
$3D$	−0.000 354 39(5)	

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